Exercise 1 Properties of polymers: coil-globule transition and Flory's model

A polymer chain in solution can either adopt an expanded coil configuration or a collapsed globular configuration. The crossover condition is usually called the *Flory θ-point*. The transition of the polymer state can be rationalized using an ideal model, in which the polymers act like ideal chains, i.e., the inter-monomer and solvent-chain interactions cancel each other out so the polymer configuration is purely entropy driven.

Consider a model of ideal polymer made of N monomers linked by a spring of spring constant $k = 3k_BT/b^2$, with b the average bond lengths. Given $\mathbf{r}_j$ the position of the j-th monomer, the potential determining the polymer state and the corresponding (normalized) probability distribution, read

$$V_N(\mathbf{r}_1...\mathbf{r}_N) = \frac{1}{2}k\sum_{j}^{N-1}|\mathbf{r}_{j+1} - \mathbf{r}_j|^2 \ , \tag{1}$$

$$P(\mathbf{r}_1...\mathbf{r}_N) = \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left[-\beta V_N(\mathbf{r}_1...\mathbf{r}_N)\right] \ . \tag{2}$$

To define whether the polymer is in an expanded or a collapsed state, a commonly used parameter is the so-called *radius of gyration* R_g, which measures how spread out the polymer is with respect to its center of mass. It is defined as follows:

$$R_g^2 = \frac{1}{N}\left\langle \sum_{j}^{N}|\mathbf{r}_j - \mathbf{r}_{CM}|^2 \right\rangle. \tag{3}$$

The value of this parameter in the ideal (θ-solvent) condition is important for characterizing the transition between the two polymer phases. Computing the ensemble average with the ideal chain probability distribution previously defined, one gets

$$R_g^2 = \frac{1}{6}Nb^2 \tag{4}$$

which implies $R_g \sim bN^{1/2}$. This result represents the ideal limit with $\nu = \frac{1}{2}$ of the general Flory's formula $R_g \sim bN^\nu$, where ν is the *Flory exponent*. In the case of an attractive potential, R_g is expected to be smaller than that of an ideal polymer, so $\nu < 0.5$. Conversely, for a repulsive potential $\nu > 0.5$. We will see both numerically (now) and analytically (next Monday) that when considering a hard sphere (repulsive) interaction potential, or similarly a high temperature regime, the expected Flory exponent is $\nu \sim 3/5$. For a general potential with both attractive and repulsive components, ν also depends on the thermodynamic conditions such as temperature and pressure.

An other important quantity of polymer physics is the end-to-end distance $\mathbf{R} = \mathbf{r}_N - \mathbf{r}_1$. In the ideal case, this variable behaves as a random walk with mean $\langle \mathbf{R} \rangle = 0$ and variance $\langle R^2 \rangle = b^2N$. These definitions allow us to define a macroscopic Gaussian probability distribution associated with observing the polymer with an the end-to-end distance R,

$$P(R) = \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left[-\frac{3}{2}\frac{R^2}{\langle R^2\rangle}\right] = \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left[-\frac{3}{2}\frac{R^2}{b^2N}\right] \ , \tag{5}$$

which corresponds to a conformational entropy

$$S(R) = S_0 + k_B \ln P(R) = S_0 - \frac{3k_B}{2}\frac{R^2}{b^2N}. \tag{6}$$

In this exercise we aim to study the basic polymer properties described above by analyzing the results of a classical MD simulation. As a simplified description of a polymer, we consider here a single chain in vacuum consisting of 100 identical monomers (beads) linked by a harmonic potential. A Lennard-Jones interaction between monomers is also included, and MD simulations are carried out at different temperatures.

(a) In the assignment folder, there are a series of trajectory files "polymer_N100_T_ ∗ .pdb" generated at temperatures ranging from 0.5 to 4.4 (Lennard-Jones units). Open them using VMD (e.g. type vmd nameofthefile) and visualize the motion of the polymer as a function of time. Do you see a change in the shape of the polymer as the temperature is increased? Provide a qualitative explanation.

(b) In order to quantify how coiled a polymer is, one can calculate the the end-to-end distance $R = |\mathbf{r}_N - \mathbf{r}_1|$. One option is to select the ends of the polymer (index 1 and 100), define a bond and record its length. Plot the time evolution of end-to-end distance and calculate its mean square value $\langle R^2 \rangle = \frac{1}{N}\sum_{i=1}^{N} R_i^2$ for each temperature T. Plot $\langle R^2 \rangle$ as a function of T. Can you infer the cross-over temperature between the coiled and the globular state from these plots?

(c) You should find files named "poly_ ∗ .data" in the assingment folder which contain the potential energy of the system as a function of simulation time at different temperatures. Plot the average potential energy U as a function of the temperature T. How can you explain the different shapes between $U(T)$ and $\langle R^2 \rangle (T)$? *Hint: think about what you learned about phase transitions.*

(d) How do you expect the curves for $U(T)$ and $\langle R^2 \rangle (T)$ to change for $N \to \infty$?

(e) Using the highest temperature provided, compare simulations with polymers having a different number of monomers and estimate the Flory exponent ν by plotting $\sqrt{\langle R^2 \rangle}$ as a function of N. Is the result consistent with your expectations? *Hint: consider that data points are affected by a (considerable) statistical error!*

(f) According to the previous discussion, does the polymer behave as an ideal chain at the crossover temperature?

The End.